Geological Survey
of Canada

Current Research
2001-E11

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2001

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Catalogue No. M44-2001/E11E
ISBN 0-660-18593-8

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102-00517/

A comparison of seven methods for analysis of carbon in soils

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Girard, I. and Klassen, R.A., 2001: A comparison of seven methods for analysis of carbon in soils; Geological Survey of Canada, Current Research 2001-E11, 9 p.

Abstract: Comparison of seven analytical protocols used for carbon analysis in soils indicates differences that relate to mineralogy, carbon content, and analytical equipment design and operation. For routine analyses of surficial geological materials containing either inorganic or organic carbon forms, or both, an appropriate method is based on thermal decomposition and oxidation of the sample with carbon released as carbon dioxide analyzed by infrared spectrometry using a Leco CR-412 instrument. The procedure requires analyses of two sample splits. One split is subjected to high-temperature (1350°C) combustion to determine its total carbon content. The second split is initially oxidized at low temperature (500°C) to remove volatile and readily oxidized carbon forms (organic), after which the remaining carbon forms (inorganic) are then determined through high-temperature combustion and carbon dioxide analyses.

Résumé : La comparaison de sept protocoles analytiques pour l'analyse du carbone dans les sols démontre des variations qui sont liées à la minéralogie, à la teneur en carbone, ainsi qu'aux méthodes et à l'instrumentation employées. Aux fins d'analyse de routine de matériaux géologiques de surface contenant du carbone inorganique et/ou organique, la méthode recommandée repose sur la décomposition thermique et l'oxydation de l'échantillon, accompagnées de l'analyse du carbone libéré sous forme de dioxyde de carbone par spectrométrie infrarouge à l'aide de l'appareil Leco CR-412. Cette procédure requiert l'analyse de deux aliquots. Le premier est soumis à une combustion à haute température (1 350 °C) afin de déterminer la teneur totale en carbone. Le deuxième est tout d'abord oxydé à basse température (500 °C) afin d'éliminer les formes volatiles et facilement oxydables de carbone (organiques), après quoi la détermination des formes résiduelles de carbone (inorganiques) est réalisée par une combustion à haute température et l'analyse du dioxyde de carbone.

INTRODUCTION

For geochemical, agricultural, and environmental studies, carbon is analyzed to establish the organic matter content, mineralogy, and provenance of soils, and the effects of weathering and soil formation processes. In surficial deposits, carbon varies widely in form, residence site, and concentration. Organic carbon occurs in compounds ranging from undecomposed wood and vegetation, to humus, peat, coal, and black shale. Inorganic carbon is bound in carbonate minerals, principally calcite and dolomite, but it also occurs in ankerite, magnesite, and graphite, among others. In addition to primary, rock-forming minerals, soil carbonate also occurs in secondary precipitates, commonly calcite. Physical and chemical differences among the carbon forms lead to different rates of thermal and chemical decomposition. Hence, carbon analyses results can reflect geological and mineralogical factors as well as analytical protocol.

A variety of analytical approaches that are commonly used report carbon as: 1) 'total', 2) 'organic', bound with H and N, and 3) 'inorganic', bound in carbonate minerals. Through comparison of seven analytical methods, this report illustrates the effects of both methodology and geological factors on soil carbon analyses results. It also indicates a method appropriate for the routine analyses of surficial sediments and soils. The work was carried out in support of the Sedimentology Laboratory of the Terrain Sciences Division, and is based on samples submitted to the laboratory for carbon analyses as part of several GSC projects. In the protocols investigated here, carbon analyses are based two determinations, one for total carbon and the other for one of the two forms. Using the two analytical determinations, the second carbon form is determined by calculation, assuming total carbon equals the sum of organic and inorganic carbon.

METHODS

Thirty-six samples of Lake Winnipeg and Red River sediments from Manitoba, sand dunes from Saskatchewan, and humus and peat from Nunavut were analyzed using different analytical protocols. The samples were chosen to represent a wide range of organic matter contents and varied geological provenance. To establish the effects of carbonate mineralogy, Chittick analyses for calcite and dolomite (Dreimanis, 1962) were carried out on Lake Winnipeg and on Saskatchewan samples. The organic carbon-rich (>30 wt %) Nunavut samples, which overlie Canadian Shield basement bedrock, are not known to contain carbonate minerals.

Seven analytical protocols are compared (Fig. 1). For all samples, total carbon content (TotC, Table 1) was determined by high temperature (1350°C) combustion and infrared spectroscopic analysis of the evolved carbon dioxide gas (Leco CR-412 carbon analyzer; Leco Corporation (1987)). The differences among methods principally relate to the means by which a particular carbon form – organic or inorganic, is determined on a second sample split. In three methods (methods 1, 2, 5; Fig. 1), organic carbon is directly determined through thermal decomposition and carbon dioxide analyses. In methods 1 and 2, organic carbon is released through low-temperature combustion (Leco 740°, 840°C), and in method 5 (acid residue) it is released by high-temperature combustion (Leco 1350°C) after an acid pretreatment to remove inorganic carbonate carbon. In three other methods (methods 4, 6, 7, Fig. 1) inorganic carbon is analyzed either directly through wet-chemical (50% HCl) decomposition of carbonate minerals and infrared spectroscopic analysis at room temperature (acid evolution, method 4), or indirectly through high-temperature decomposition of carbonate minerals after a pretreatment to remove organic carbon (methods 6, 7; Fig. 1). The pretreatments include either wet-chemical oxidation with hydrogen peroxide (peroxide residue, method 6) or low-temperature (500°C) oxidation (LOI 500, method 7). In the seventh procedure (proton balance, method 3; Fig. 1), inorganic carbon is determined by proton balance calculations that assume complete acid neutralization due to carbonate (calcite, dolomite) reaction.

The following is a summary description of the analytical protocols used to determine the organic and inorganic carbon forms (Fig. 1).

LECO (840), method 1

Organic carbon released through combustion at 840°C for 120 s or less is determined as carbon dioxide through infrared spectroscopy (Wang and Anderson, 1998).

Method	1	2	3	4	5	6	7
	Leco 840	**Leco 740**	**Proton balance**	**Acid evolution**	**Acid residue**	**Peroxide residue**	**LOI 500**
Organic (OC)	**Leco 840°C**	**Leco 740°C**	OC=TotC-IC	OC=TotC-IC	**Leco 1350°C (after acid pretreatment)**	OC=TotC-IC	OC=TotC-IC
Inorganic (IC)	IC=TotC-OC	IC=TotC-OC	**Proton balance**	**Acid evolution**	IC=TotC-OC	**Leco 1350°C (after peroxide pretreatment)**	**Leco 1350°C (after 500°C pretreatment)**
	Carbon form analyzed						
	TotC = Total carbon (Leco 1350°)						

Figure 1. *Summary of carbon analyses methods.*

Table 1. Analyses data for total carbon (TotC) and organic (OC) and inorganic (IC) carbon determined by seven analytical protocols. Method numbers are keyed to Figure 1.

																	Chittick		
Sample no.	Area	TotC	OC1	OC2	OC3	OC4	OC5	OC6	OC7	IC1	IC2	IC3	IC4	IC5	IC6	IC7	%Cal	%Dol	%IC
1	Nunavut	23.0	12.8	19.2	22.7	22.9	–	23	22.4	10.2	3.8	0.3	0.1	–	0.0	0.6	–	–	–
2	Nunavut	38.6	36.9	39.3	38.5	38.6	–	–	38.5	1.7	-0.7	0.1	0.0	–	–	0.1	–	–	–
3	Nunavut	40.2	39.1	38.8	40.1	40.2	–	–	40.1	1.1	1.4	0.1	0.0	–	–	0.1	–	–	–
4	Nunavut	43.2	41.2	42.4	43.0	43.2	–	–	43.0	2.0	0.8	0.2	0.0	–	–	0.2	–	–	–
5	Nunavut	45.5	43.3	40.5	45.5	45.5	–	–	45.5	2.2	5.0	0.1	0.0	–	–	0.0	–	–	–
6	Nunavut	36.5	34.9	35.3	36.4	36.5	–	–	36.5	1.6	1.2	0.1	0.0	–	–	0.0	–	–	–
7	Nunavut	44.9	43.0	41.5	44.8	44.9	–	–	44.7	1.9	3.4	0.1	0.0	–	–	0.2	–	–	–
8	Nunavut	45.1	44.1	41.4	45.0	45.1	–	–	45.0	1.0	3.7	0.1	0.0	–	–	0.1	–	–	–
9	Nunavut	44.9	44.0	42.9	44.8	44.9	–	–	44.8	0.9	2.0	0.1	0.0	–	–	0.1	–	–	–
10	Nunavut	40.1	38.8	38.7	40.0	40.1	–	–	40.0	1.3	1.4	0.1	0.0	–	–	0.1	–	–	–
11	Nunavut	33.0	31.7	29.9	32.9	33.0	–	–	32.9	1.3	3.1	0.1	0.0	–	–	0.1	–	–	–
12	Nunavut	41.6	41.2	41.4	41.6	41.6	–	–	41.6	0.4	0.2	0.0	0.0	–	–	0.0	–	–	–
13	Nunavut	46.9	46.2	45.4	46.9	46.9	–	–	46.9	0.7	1.5	0.0	0.0	–	–	0.0	–	–	–
14	Red River, Man.	2.9	0.8	0.0	1.0	1.0	–	0.3	0.9	2.1	2.9	1.9	1.9	–	2.6	2.0	–	–	–
15	Red River, Man.	3.0	0.7	0.0	1.1	1.0	–	0.5	1.0	2.3	3.0	1.9	2.0	–	2.5	2.0	–	–	–
16	Red River, Man.	3.1	0.9	0.0	1.2	1.1	–	0.5	1.0	2.2	3.1	1.9	2.0	–	2.6	2.1	–	–	–
17	Red River, Man.	3.2	0.4	0.0	1.1	0.6	–	0.4	0.6	2.8	3.2	2.1	2.6	–	2.8	2.6	–	–	–
17(Duplicate)	Red River, Man.	3.2	0.4	0.0	0.9	0.6	–	0.1	0.7	2.8	3.2	2.3	2.6	–	3.1	2.5	–	–	–
18	Red River, Man.	3.3	0.6	0.0	1.1	0.5	–	0.3	0.8	2.7	3.3	2.2	2.8	–	3.0	2.5	–	–	–
19	Red River, Man.	3.4	0.5	0.0	1.2	0.9	–	0.2	0.6	2.9	3.4	2.2	2.5	–	3.2	2.8	–	–	–
20	Sand dunes, Sask.	0.9	0.2	0.0	0.3	0.2	–	0.2	0.3	0.7	0.9	0.6	0.7	–	0.7	0.6	3.45	1.62	0.63
21	Sand dunes, Sask.	2.8	0.2	0.0	0.4	0.3	–	0.2	0.8	2.6	2.8	2.4	2.5	–	2.6	2.0	18.92	1.35	2.45
22	Sand dunes, Sask.	7.8	2.7	1.6	3.2	3.0	–	0.8	3.2	5.1	6.2	4.6	4.8	–	7.0	4.6	32.3	4.57	4.47
23	Sand dunes, Sask.	0.8	0.3	0.0	0.4	0.4	–	0.3	0.5	0.5	0.8	0.5	0.4	–	0.5	0.3	3.26	0.45	0.45
23G(carbon)	Sand dunes, Sask.	6.7	0.6	0.0	6.2	6.3	–	6.3	0.7	6.1	6.7	0.5	0.4	–	0.4	6.0	–	–	–
24	Sand dunes, Sask.	3.6	0.5	0.0	0.5	0.4	–	0.5	0.6	3.1	3.6	3.1	3.2	–	3.1	3.0	22.0	0.67	2.73
25	Sand dunes, Sask.	1.3	0.5	0.0	0.7	0.7	–	0.6	0.7	0.8	1.3	0.6	0.6	–	0.7	0.6	2.51	1.57	0.51
26	Lake Winnipeg, Man.	2.8	0.3	0.0	0.2	0.2	0.3	0.0	0.2	2.5	2.8	2.6	2.6	2.5	2.8	2.6	5.6	15.3	2.67
27	Lake Winnipeg, Man.	3.0	0.1	0.0	0.3	0.4	0.2	0.2	0.2	2.9	3.0	2.7	2.6	2.8	2.8	2.8	7.8	14.1	2.78
28	Lake Winnipeg, Man.	2.9	0.3	0.0	0.2	0.1	0.3	-0.1	0.2	2.6	2.9	2.7	2.8	2.6	3.0	2.7	9.5	12.2	2.76
28(Duplicate)	Lake Winnipeg, Man.	2.9	0.3	0.0	0.2	0.1	–	-0.1	0.2	2.6	2.9	2.7	2.8	–	3.0	2.7	–	–	–
29	Lake Winnipeg, Man.	8.2	0.4	0.0	2.8	0.0	0.3	0.1	0.3	7.8	8.2	5.4	8.2	7.9	8.1	7.9	14.6	45.4	7.67
30	Lake Winnipeg, Man.	6.7	0.6	0.0	1.3	0.3	0.5	0.0	0.7	6.1	6.7	5.4	6.4	6.2	6.7	6.0	–	–	–
31	Lake Winnipeg, Man.	8.7	0.2	0.0	3.4	-0.1	0.1	-0.1	0.4	8.5	8.7	5.3	8.8	8.6	8.8	8.3	15.8	50.9	8.54
JDo-1	Dolomite 12.8*	12.8	0.2	0.0	2.1	-0.3	0.0	0.3	0.3	12.6	12.8	10.7	13.1	12.8	12.5	12.5	–	–	–
JLs-1	Calcite 12.0*	12.0	0.0	0.0	0.0	-0.4	0.0	-0.1	0.0	12.0	12.0	12.0	12.4	12.0	12.1	12.0	–	–	–
SO-1	Soil 0.3*	0.3	0.2	0.0	0.2	0.3	0.5	0.3	0.3	0.1	0.3	0.1	0.0	-0.2	0.0	0.0	0.7	0.5	1.4
SO-2	Soil 4.8*	4.8	4.7	4.5	4.7	4.7	4.4	3.9	4.8	0.1	0.3	0.1	0.1	0.4	0.9	0.0	0.8	0.5	1.6
SO-3	Soil 6.7*	6.7	0.3	0.0	0.8	-0.1	0.5	0.0	0.2	6.4	6.7	5.9	6.8	6.2	6.7	6.5	22.4	28.3	6.4

* Expected total carbon value for reference material

LECO (740), method 2

Organic carbon released through Leco combustion at 740°C for 120 s or less is determined as carbon dioxide through infrared spectroscopy (Wang and Anderson, 1998).

Proton balance, method 3

Inorganic carbon is determined by adding a measured aliquot of 0.4 M acetic acid to the sample. Through proton balance calculations, the resulting pH change is used to determine carbon present in reactive carbonate minerals (Loeppert et al., 1984).

Acid evolution, method 4

Inorganic carbon lost through decomposition of carbonate minerals in 50% HCl is directly estimated through analyses of carbon dioxide by infrared spectroscopy at room temperature (Leco CR12), after removal of chlorine fumes by bubbling through a copper sulphate solution (Abbey, 1979; Bouvier and Abbey, 1980; Johnson and Maxwell, 1981; P.G. Bélanger, unpub. laboratory procedures, 1987).

Acid residue, method 5

Organic carbon is measured by high-temperature Leco combustion (1350°C) and infrared carbon dioxide detection (Leco CR-412) after pretreatment with 50% HCl. The pretreatment removes inorganic carbon in carbonate minerals. Prior to organic carbon analyses, the treated sample is washed, dried, and reweighed. Chlorine fumes in the residue are removed with an on-line potassium iodide filter (Saikkonene and Rautiainen, 1990). Acid residue analyses were only carried out on Lake Winnipeg and 'soil reference' samples.

Peroxide residue, method 6

Organic matter is first removed through oxidation with strong (30 wt %) hydrogen peroxide, and the residual inorganic carbon then analyzed through high-temperature (1350°C) combustion (Black, 1965; Kunze and Dixon, 1986; Carter, 1993). Peroxide residue analyses were carried out on inorganic samples only.

Loss-on-ignition (LOI 500), method 7

The sample is first heated to 500°C and held at that temperature for one hour to remove organic carbon. Residual inorganic carbon remaining in the pretreated sample is determined through high-temperature (1350°) Leco combustion and carbon dioxide analyses.

Calibration and quality controls

For total carbon analyses (TotC, Table 1), calibration of the Leco instrument was performed using 350–500 mg of pure calcium carbonate. For inorganic carbon (IC, Table 1) analyses using methods 3, 5, 6, and 7, calibration of the Leco instrument and of the pH meter was also performed using 350–500 mg of pure calcium carbonate. For inorganic carbon analyses using method 4, 300 mg of barium carbonate was used for the calibration. For organic carbon (OC, Table 1) in methods 1 and 2, pure sugar and alfalfa (Leco PN 502-273) were used as calibration standards.

Quality control is based on analysis of two duplicate samples, three certified reference standards (Canadian Certified Materials SO-1, SO-2, SO-3) (Terashima, 1988), and rock reference standards of pure calcite (JLs-1) and dolomite (JDo-1) from the Geological Survey of Japan (Terashima, 1988; Ando et al., 1990). For the reference materials, the published carbon analyses are total; no analytical data for organic-inorganic subdivisions are available. In addition, one sample (sample 23G (carbon)) was spiked with pure carbon to investigate the effects of carbon in the form of graphite on analytical outcomes.

RESULTS AND DISCUSSION

For geological materials, weight loss is potentially a more unreliable indicator of carbon content than infrared spectrometry, which is a direct indicator for carbon as carbon dioxide. Weight changes can be due to 1) loss of elements other than carbon through volatilization and oxidation, including hydrogen, nitrogen, sulphur, and oxygen; 2) loss of bound water and hydroxyl molecules in minerals and in iron and manganese oxy-hydroxides; and 3) mineral decomposition, including both carbonate and noncarbonate minerals (Jackson, 1969). Serpentine, for example, decomposes in the 300–900°C temperature range (Jackson, 1969, Table 6-2, p. 300). The degree to which elements are lost reflects their form, concentration, and mineral residence sites, as well as the time and temperature of combustion. In methods 5, 6, and 7, weight determinations made after pretreatment, prior to total Leco combustion, establish the basis for calculating the mass of carbon lost as carbon dioxide as a sample weight per cent.

In the following discussion, analytical method (methods 1–7 above), analytical results, and carbon form (inorganic - IC; organic - OC) are keyed to Table 1.

In sediment samples, inorganic carbon (IC4) varies from about 2.5–8.5 weight per cent in Lake Winnipeg sediments; 2–2.5 weight per cent in Red River sediments; 0.5–5 weight per cent in Saskatchewan sand dunes; and does not occur in Nunavut peat (Fig. 2a). Organic carbon is low (<2%) in all prairie samples, and is much greater in Nunavut peat (20–50 wt %) (Fig. 2b).

For Leco CR-412 infrared spectrometry, used in this study, analytical precision is estimated as the sum of ±0.1% instrument error, and ±5% of the analytical result; the ±5% estimate is based on statistical analyses of standards analyzed by the Mineral Resources Division of the GSC. Other sources of error relate to sample loss either through vigor of reaction or losses associated with washing, drying, and weighing where pretreatment is used to remove one carbon form prior to analyses of the second (methods 5, 6, 7).

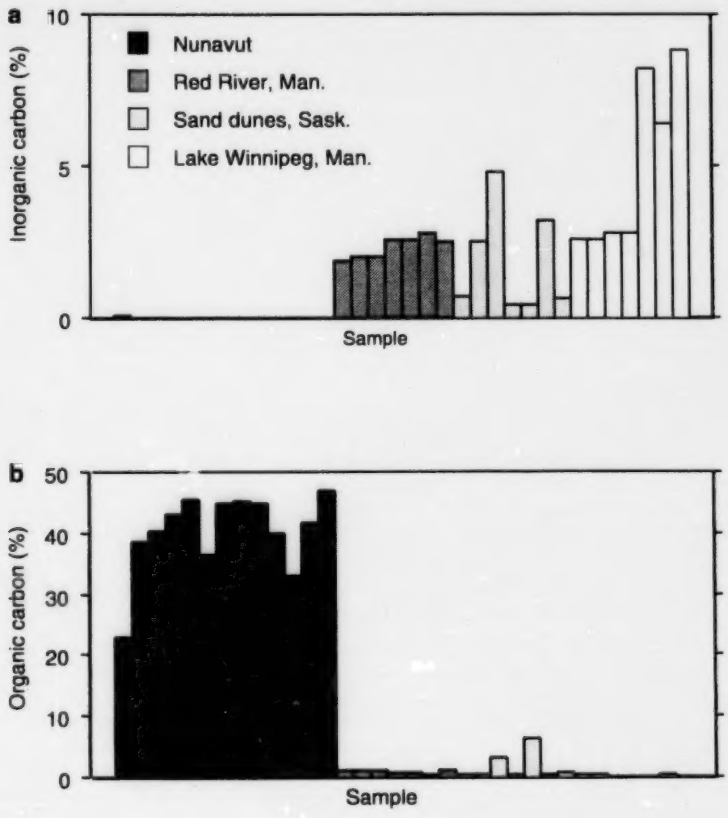

Figure 2.

*Bar chart illustrating the **a**) inorganic and **b**) organic contents determined by acid evolution (method 4) of the geological materials used for this study.*

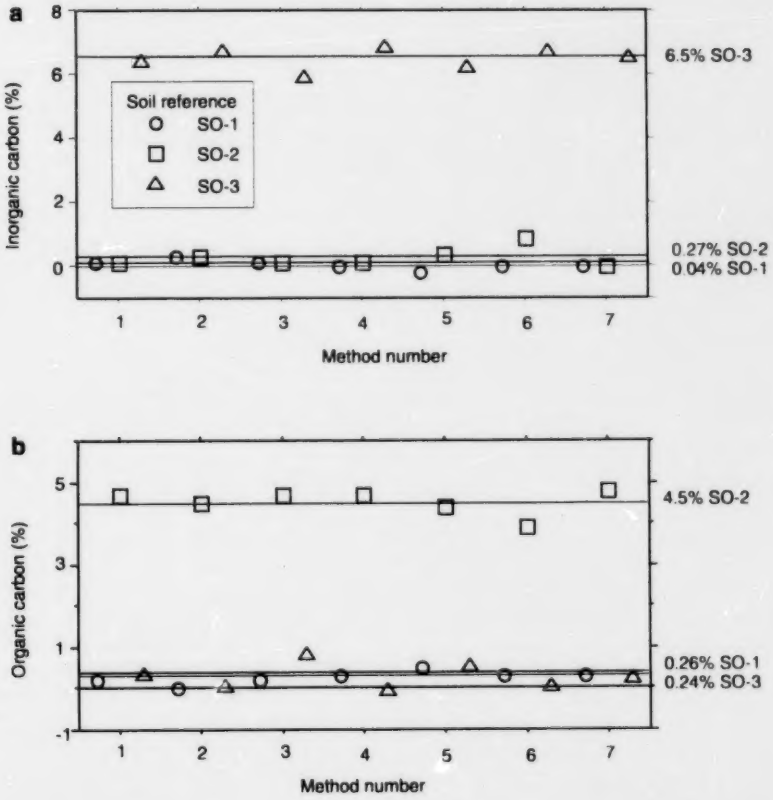

Figure 3.

*Comparison of **a**) inorganic carbon and **b**) organic carbon analyses results for three soil reference standards. Experimental average values shown by horizontal lines.*

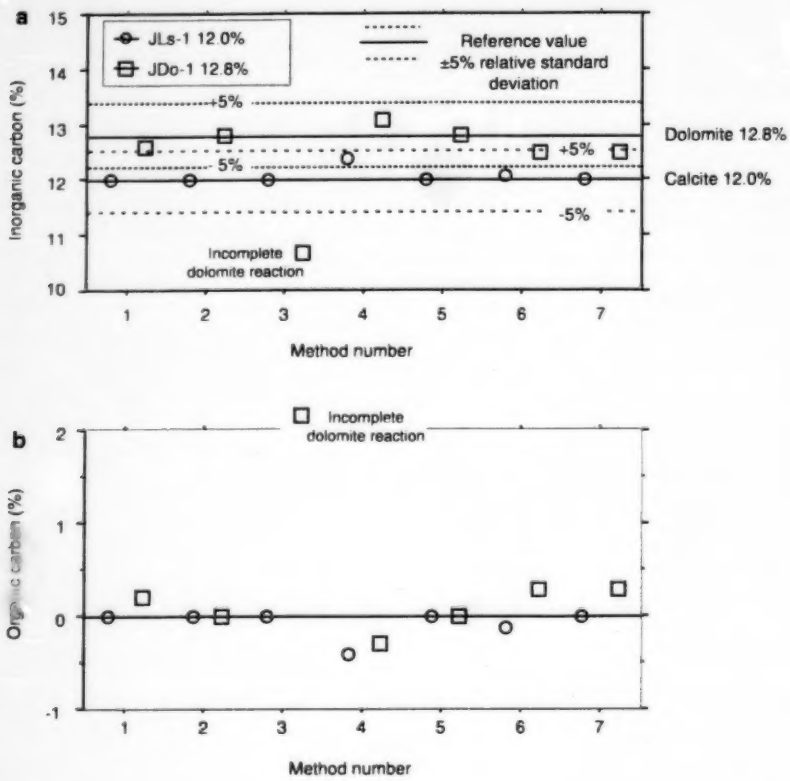

Figure 4.

*Comparison of **a**) inorganic carbon and **b**) organic carbon analyses results for calcite and dolomite reference standards JLs-1 and JDo-1 according to analytical method.*

Soil standards

For total carbon analyses of the soil standards, results were well within the expected error range (±5%) (Table 1). Standards SO-1 and SO-2 contain little (<0.1%) inorganic carbon, whereas standards SO-1 and SO-3 contain little (<0.3%) organic carbon. Standard SO-3 contains about 50 weight per cent calcite and dolomite, with the two minerals present in equivalent proportions (Table 1). For soil sample standards, the largest apparent errors are associated with proton balance (method 3) for the inorganic carbon standard (6.5%, SO-3), and with peroxide residue (method 6) for an organic carbon soil standard (4.5%, SO-2) (Fig. 3).

Reference standards

For total carbon analyses of calcite-dolomite rock reference materials (Leco combustion at 1350°C), results were within the expected error range (±5%) (Table 1; Fig. 4). The largest error is associated with the dolomite reference material analyzed by proton balance (method 3), and with both calcite and dolomite reference standards by acid evolution (method 4; Fig. 4a). For dolomite (IC3), the estimate is about 2 weight per cent less than the expected value. The low value likely reflects incomplete mineral decomposition by the weak acid, consistent with the long period of observed gas evolution (1 week). Values for IC4 are about 0.5% greater than expected for the reference materials. Organic carbon is calculated using inorganic carbon values, hence, OC4 estimates are reported as negative. The differences from reference values are attributed to the high inorganic carbon content of the reference standards and to the need to extrapolate instrument calibration curves (Leco CR12) beyond their 6% carbon upper limit. In addition, acid evolution (method 4) involves a transfer of gas to the infrared detector that represents a further, potential source of error. Methods 1, 6, and 7 indicate some organic carbon (0.2–0.3 wt %) in the dolomite reference sample (JDo-1), reflecting either partial thermal decomposition of dolomite at 840°C and 500°C, or wet-chemical oxidation (Fig. 4b). The sample was held at the lower temperature (500°C) for more than one hour.

Carbon-rich samples

In the Leco furnace, the rate of carbon dioxide release is monitored to establish when oxidation is complete, and the cumulative release of carbon is determined by integrating the carbon released over time. Decomposition is deemed complete when the carbon dioxide release slows to a predetermined rate. At furnace temperatures where carbonate minerals can decompose, 740°C for dolomite and 970°C for calcite, any release of inorganic carbon would be erroneously calculated as organic. For that reason, the combustion time is limited to 120 s (Wang and Anderson, 1998). For organic-rich (>20 wt %) samples, however, it is difficult to achieve a complete combustion within the 120 s instrument time limits, and in that case unoxidized organic carbon remaining in the sample would be erroneously calculated as inorganic carbon.

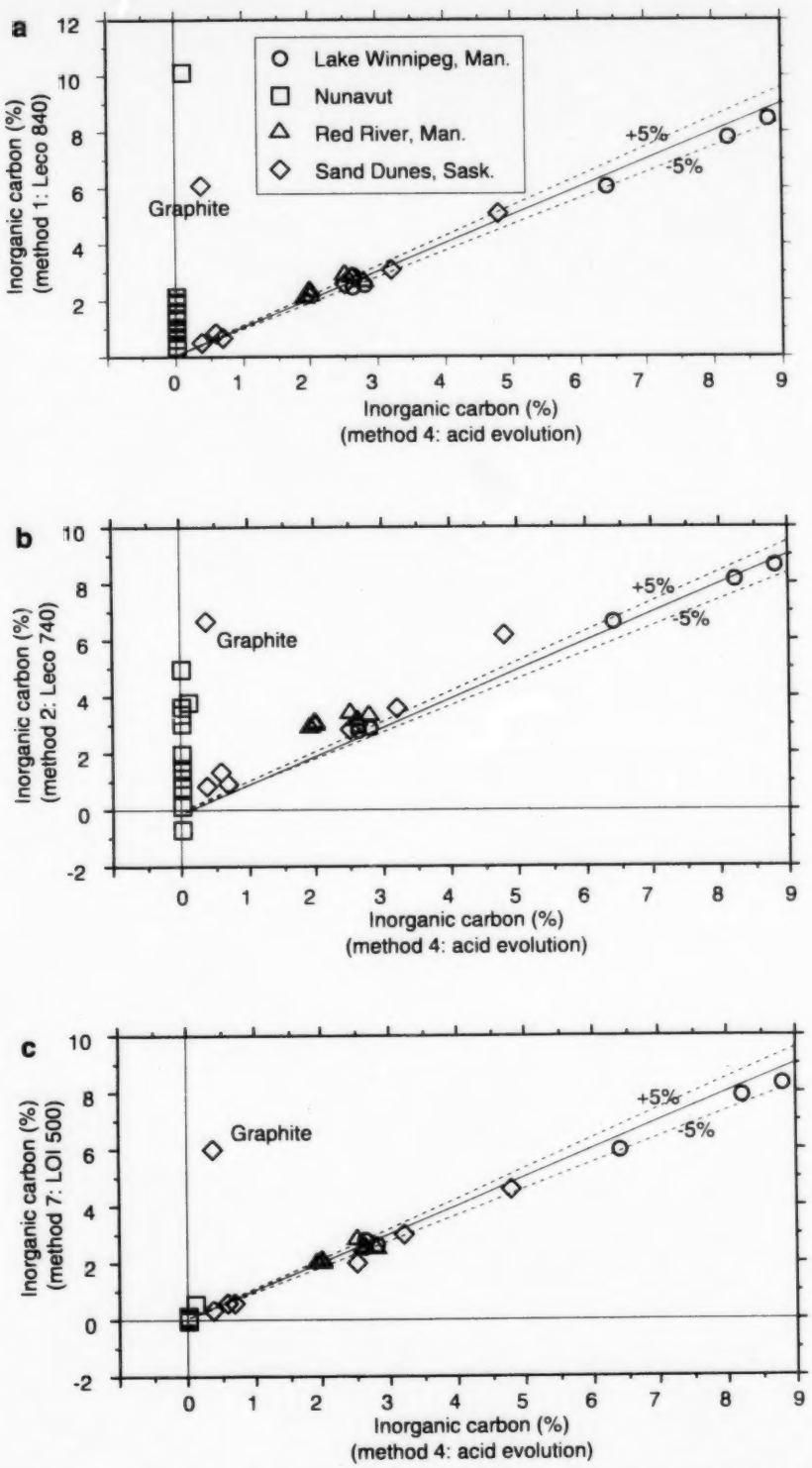

Figure 5. *Plots comparing inorganic carbon analytical results by* ***a****) Leco 840,* ***b****) Leco 740,* ***c****) LOI 500 with those by acid evolution.*

For Nunavut peat, there are significant differences among the methods in the amount of organic-inorganic carbon determined (Fig. 5). The differences are greatest for analyses based on Leco combustion (methods 1, 2; Leco 840, 740). Peat samples are reported to contain 0–2.5 weight per cent (Leco 840) and 0–5 weight per cent (Leco 740) inorganic carbon, presumably reflecting incomplete organic carbon combustion. In contrast, where organic carbon is oxidized at 500°C over a longer period of time (60 minutes), oxidation is either complete or nearly so (LOI 500, method 7), with inorganic carbon contents indicated to be less than 0.1% (Fig. 5c; Table 1). Method 4 indicates Nunavut peat samples contain no inorganic carbon, a result that is consistent with their geological context in noncarbonate terrain of the Canadian Shield. The relative standard deviation (RSD) associated with paired analyses results (Garrett, 1969) derived from methods 4 and 7 indicates differences of ±1%, well within the estimates of analytical uncertainty associated with the Leco carbon analyzer (±5%).

Carbonate carbon-rich samples

Strong acid digestion (acid evolution, method 4) is a reliable method for estimating inorganic carbon in carbonate minerals, although it cannot be used for graphite carbon because graphite is not reactive with hydrochloric acid. Using method 4 inorganic carbon results as a comparative reference, estimates of inorganic carbon based on 740°C oxidation (method 2) are about 0.2–1% greater than those of 840°C (method 1) (Fig. 5a, b). The results indicate oxidation of organic carbon at 840° is more complete than at 740°C; unburned organic carbon is not subtracted from the total carbon content in the estimation of inorganic carbon and hence is included as 'inorganic'. Inorganic carbon estimates derived from methods 1 and 2 are all either equivalent to or greater than those obtained with method 4. Consequently, there is no indication for thermal decomposition of dolomite, which would increase estimates of organic carbon. Dolomite occurs in Lake Winnipeg and Saskatchewan samples (Table 1), and is assumed present, albeit in unknown proportions, in the other prairie samples. Inorganic carbon determined by acid evolution and by LOI 500 are equivalent (±5%) to those estimated by Chittick analyses (Fig. 6).

Limitations

Until acquisition of the Leco CR-412, the Sedimentology Laboratory used the acid residue (method 5) to estimate carbon content using an infrared CO_2 detector. Two sample splits were analyzed by high-temperature combustion in a Leco CR-12 furnace; one was first treated with strong hydrochloric acid to drive off carbon in carbonate minerals and leave an organic residue, and the second was burned untreated. Using this protocol, fine-grained particulate and dissolved material was lost by leakage through the porous ceramic boat containing the sample. The mass lost through leakage was included in the estimates of organic carbon lost through combustion, erroneously increasing inorganic carbon estimates. Chlorine generated by the acid residue method is not removed through pretreatment and, hence, corrodes the infrared cell and furnace lining leading to increased operational expenses. The on-line chlorine filter (KI) needs to be frequently changed, and a quartz sample boat, which is more expensive than the standard ceramic boat, must be used to minimize chlorine retention. Furthermore, the effervescence can lead to a loss of sample material from the reaction boat.

The proton balance method (method 3) requires operator care and a long period of reaction time (days) to ensure complete digestion of carbonate minerals. Where the reaction time exceeds 24 hours hydrogen ions can also be consumed by soil ion exchange, leading to overestimation of inorganic carbonate carbon (Loeppert et al., 1984). Incomplete acid decomposition of dolomite leads to underestimation of inorganic carbon. The dolomite reference standard (JDo-1), for example, effervesced in acetic acid for more than one week without achieving complete decomposition, resulting in inorganic carbon analyses results 1–2% lower than determined by other methods (Fig. 4).

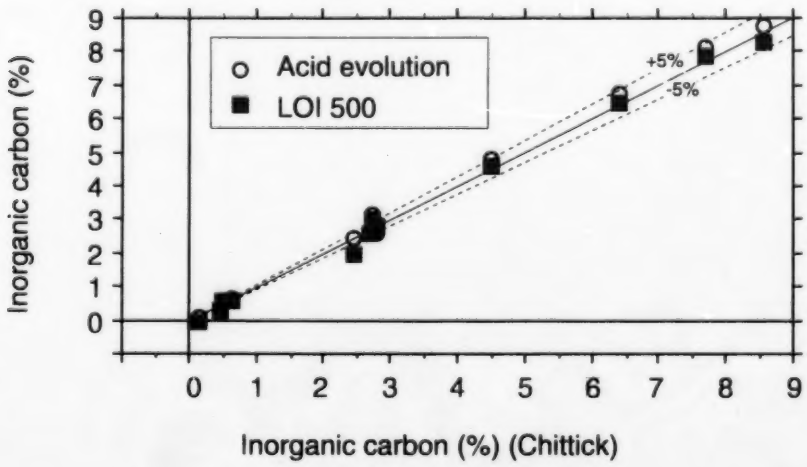

Figure 6.

An X-Y plot comparing inorganic carbon analyses by the Chittick method with results determined by acid evolution and by LOI 500. For carbon contents less than 10% the data are within ±5% uncertainty expected.

The acid evolution method (method 4) removes chlorine by bubbling evolved gases through copper sulphate solution prior to carbon analyses. Although analytical results are both accurate and reproducible, laboratory operations are more difficult to adapt to processing large sample batches.

Organic matter is readily oxidized by hydrogen peroxide (method 6) (Black, 1965; Kunze and Dixon, 1986; Carter, 1993). For organic-rich samples, however, the reaction time can extend over several days, and residue is difficult to remove from the walls of the reaction vessel.

Graphite

In methods 1, 2, and 7, graphite is reported as inorganic carbon (e.g. Fig. 5), whereas in methods 3, 4, 5, and 6 it is reported as organic carbon (Table 1; Fig. 5). Although the differences can present problems for geological research, they indicate a potential basis for developing a graphite analyses methodology.

CONCLUSIONS

Loss-on-ignition (LOI 500) (method 7) and acid evolution (method 4) provide analytical results that are well within the limits of uncertainty expected of Leco instrument operation (±5%). The results are consistent with what is known of sample mineralogy, and closely approximate the published values for reference standards. In addition, both methods accommodate a wide range of sample organic matter contents, making them suitable for routine analyses of geological samples. Of the two methods, LOI 500 is considered the best choice for technical reasons related to laboratory operation. The LOI method can be more readily adapted to processing large batches of samples, and provides supplementary information related to weight loss at 500°C, information that can be used to discriminate among organic materials. The removal of chlorine generated by acid evolution requires greater operator involvement and equipment maintenance, and limits its application to the Leco CR-12 analyzer. A potential drawback for routine use of the LOI 500 method is that it can indicate low inorganic carbon contents (<0.1 wt %) where none occur, especially for organic-rich samples where some residual organic carbon is likely to remain following combustion.

ACKNOWLEDGMENTS

We would like to thank Inez Kettles for her review and constructive comments. We are also grateful to Mylène Pilon for carrying out part of the analyses, the Analytical Laboratories of the Mineral Resources Division for providing sample analyses through acid evolution method, and to Peter Bélanger for insightful comments throughout the project.

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Geological Survey of Canada Project 950032